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Utilization of Near Infrared (NIR) Spectrometry for Detection of Glass in the Waste-based Fuel

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Abstract

This paper presents the results of experimental measurements and multivariate statistical modeling concerning detection of soda-lime glass using near infrared (NIR) spectrometry technique. The purpose is to test if the glass is quantitatively detectable in a waste-based material and to assess what method of spectral data pretreatment is the most suitable in order to develop prediction models. The experiments were performed on six test samples containing a specific amount of glass distributed in background material. Pretreatment methods such as normalization and first and second derivatives were applied on the acquired absorbance spectral data. Principal component analysis (PCA) was employed in order to describe the relationship between pretreated data and the amount of glass in the test samples. Subsequently, principal component regression (PCR) was utilized for the development of prediction models. The results from the models show strong correlation between the pretreated data and the glass content. The most promising results were obtained from the model based on 1st derivative pretreatment when only absorbance spectral data from selected wavelengths are included.

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Keywords: Near infrared spectroscopy; soda-lime glass; material detection; multivariate data analysis

1. Introduction

The presence of glass in a waste-based fuel, which is intended for incineration in fluidized bed boilers, causes increased risk of operational problems [1]. This is due to the poor heat resistance of glass. The most

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frequently found glass material in municipal solid waste (MSW) and industrial solid waste (ISW) is a soda-lime glass containing mostly SiO_2 [2]. Glass material combined with elements such as K, Na, Cl, S, Si, and P from the fuel form low-melting compounds. These compounds deposit on the bed particles (silica sand; i.e. SiO_2 in the form of quartz), forming agglomerates and cause bed defluidization which result in a malfunction or failure of the combustion equipment followed by the necessity of replacing the bed material. Furthermore, when glass is heated to temperatures close to its melting point, a high viscous silicate phase can form, which causes clogging problems during sand/ash extraction and the boiler may need an unscheduled shut down [3]. This leads to increased operating cost for the facility and environmental issues due to the increased production of used bed material and enlarged emissions during operation, startup and shutdown of the boiler. These problems can be minimized by improving process monitoring and control followed by appropriate operational measures. Therefore, the challenge is to find a method for rapid and reliable on-line characterization of the fuel fed into the boiler.

One of the methods used for on-line non-destructive solid material characterization is near infrared (NIR) spectroscopy. This method is based on vibrational spectroscopy, which measures the interactions of electromagnetic NIR radiation with the chemical bonds of the sample constituents at different wavelengths. The NIR spectroscopy technique is used widely and for many years in the field of food science and engineering [4, 5] as well as the pharmaceutical industry [6-8] for quality monitoring. It is also extensively used in forestry as well as the pulp and paper industry for identification of wood and characterization of its properties [9-12] and for measurements of pulp properties [13, 14]. Moreover, it's also used in waste management for many applications such as monitoring of the landfilled material, separation of recyclables, recovery of biodegradable materials etc. [15]. In the field of heat and power production it is mostly used for measurement and prediction of moisture, ash content and calorific value of the fuel which is supplied to the boiler [16, 17]. The literature review presented shows that the on-line industrial applicability of NIR spectroscopy is possible and sufficiently reliable. However the on-line detection of the glass in material has been so far limited to research of ceramic glass detection in glass recycling plants [18]. Hence, the authors argue that the following questions need to be addressed:

Is it possible to quantitatively detect glass in biomass-based material using a near-infrared spectrophotometer? If yes, how can we improve the performance of a prediction model that feeds into a power plants control systems?

The optical properties of commercial glass have been studied in several publications [19, 20] and they relate to the concentration of contaminants in the glass. The spectral patterns of glass materials differ substantially from those of biomass-based materials and thus we may assume that imperfect glass might be detectable. In addition to it, if we succeed with quantitative detection, the model performance can be improved by using data pre-processing techniques, which are discussed in [21]. Their suitability, among others, depends on the optical principle of the instrument used and the properties of the material.

Therefore, the first objective of this paper is to test if the soda-lime glass material is detectable in biomass-based fuel by using NIR spectroscopy. The second objective is to develop multivariate statistical models which can describe the correlation between absorbance spectra at different wavelengths and the glass content in the fuel sample. Principal Component Analysis (PCA) shall be employed in order to identify such correlations. Input spectral data shall be pretreated in different ways in order to assess which of the pre-processing techniques is the most suitable. Multivariate predictive models for predicting glass content shall be developed using a Principle Component Regression (PCR) method.

Nomenclature

ISW	Industrial solid waste
MidIR	Middle infrared
MSW	Municipal solid waste
NIR	Near infrared
PCA	Principal Component Analysis
PCR	Principal Component Regression
R^2	Coefficient of determination
RMSEC	Root mean square error of calibration
RMSEP	Root mean square error of prediction

2. Materials and methods

2.1. Test samples

Dried pine wood shavings and white (transparent) soda-lime glass from common recycled glass bottles were used as the testing material. The typical composition of soda lime glass is (in wt%) 72 SiO_2, 14 Na_2O, 11 CaO, 1 MgO, 2 Al_2O_3 and less than 1 wt% of K_2O, Fe_2O_3, TiO_2 [22]. Wood shavings were used as background material because their properties are well understood and hence more suitable for proving that glass detection is possible. Shavings were first dried and then spread uniformly on the black tray (24 x 17 cm). The glass was crushed into pieces (shards) of approx. 5-15 mm in size and spread uniformly on the wood shavings (Fig. 1.). The possibility to distinguish the particles of glass in a visible light is rather low as illustrated through Fig. 1.

Fig. 1. Test sample containing 4 vol% of soda-lime glass

Furthermore, six test samples with specific amounts of glass were created and tagged for easy identification (Table 1). The volume percentages were used, since the spectral properties of a material are proportional to the distance which the light beam has to pass during its path through a medium (Beer–Lambert law) [23].

Table 1. Test sample composition

Sample ID No.	Amount of dry pine wood shavings (vol%)	Amount of soda-lime glass (vol%)
1	100	0
2	99.5	0.5
3	99	1
4	98	2
5	96	4
6	92	8

2.2. NIR spectra acquisition

NIR spectra were acquired using a grating NIR spectrophotometer. Each absorbance spectrum was recorded at wavelengths between 400 nm and 2500 nm (i.e. also including the range of visible light) at 2 nm intervals using the average of 32 scans. Measurement repetitions were done five times for each sample. During the measurement, samples were placed on a tray so that the tray may move horizontally in a reciprocating manner underneath the sensor at a velocity of approx. 0.1 $m \cdot s^{-1}$. This was done in order to replicate the movement of a real conveyor belt as used for transporting fuel to a boiler.

2.3. Data analysis

The data pretreatment and analysis were done using commercially available software [24]. PCA was employed in order to describe the relationship between spectral data and the sample properties. The data were pretreated prior to the analysis in order to improve subsequent multivariate regression as discussed in [21]. The mean normalization was applied, in other words each observation (different wavelengths) of the data matrix was divided by its average. Moreover, 1st derivatives with smoothening (13 smoothening points, 3rd degree polynomial) and 2nd derivatives with smoothening (13 smoothening points, 3rd degree polynomial) were applied on the spectral data using the Savitzky and Golay algorithm [25] as suggested in [26]. Then PCR was utilized for the development of prediction models. PCR is a regression analysis technique that is based on PCA. It is regressing the dependent variable on a set of independent variables based on a standard linear regression model when using PCA for estimating the unknown regression coefficients in the model [24].

3. Results and discussion

The properties of different multivariate PCR models are shown in Table 2. Both the calibration data set and the test (validation) data set are presented. The full cross validation of the model was applied in order to estimate the prediction performance of the multivariate model. The same samples are used for both model estimation (calibration) and testing (validation). Only one sample is left out of the calibration data set and the model is calibrated on the remaining data points. The values for the left-out sample are predicted and the prediction residuals are computed. The process is repeated with another subset of the calibration set, and so on until every object has been left out once (as many sub-models as there are objects) [24].

The coefficient of determination (R^2) indicates how well the data fit the statistical model. The root mean square error (RMSE) is a measure of the differences between the values predicted by the model and the value as measured. The calibration error (RMSEC) and prediction error (RMSEP) can be distinguished.

Table 2. Results of the multivariate statistical modeling

Model No.	Data pretreatment method	Set of data	Slope	Offset	RMSEC/ RMSEP	R^2 cal./ R^2 val.
1.	Mean normalization	Cal. set	0.9717	0.0728	0.4713	0.9717
		Test set	0.9654	0.0662	0.5100	0.9658
2.	1st derivative	Cal. set	0.9695	0.0784	0.4892	0.9695
		Test set	0.9442	0.1335	0.5055	0.9734
3.	2nd derivative	Cal. set	0.9833	0.0429	0.3621	0.9833
		Test set	0.8907	0.2432	0.5129	0.9679
4.	1st derivative – selected wavelengths	Cal. set	0.9901	0.0254	0.2787	0.9901
		Test set	0.9818	0.0533	0.3268	0.9876
5.	2nd derivative – selected wavelengths	Cal. set	0.9725	0.0708	0.4649	0.9725
		Test set	0.9437	0.1197	0.5170	0.9665

All developed models show strong correlation between the pretreated spectral data and the glass content (Table 2). Model No. 4 presents the best results for both validation and test data set. (RMSEC = 0.2787 vol%, RMSEP = 0.3268 vol%, $R^2_{cal} = 0.9901$, $R^2_{val} = 0.9876$). It presents error improvements i.e. RMSEC and RMSEP, 40% and 35% respectively and R^2 improvements approx. 1% compared to the model pre-treated only with mean normalization. Model No. 4 includes three principal components which explain 99% of the variation for the explicative predictor variables X (absorbance at different wavelengths) and for response variables Y (soda-lime glass content) as shown in Fig. 2.

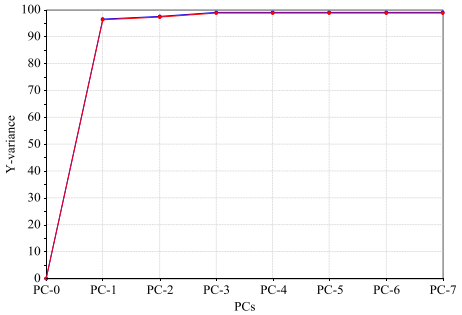

Fig. 2. Explained variance plot for response Y in model No. 4

Model No. 4 is based on 1st derivative data including only selected wavelengths. The most important wavelengths (81 variables) were selected based on the correlation loadings plot of PC-1 and PC-2 as shown in Fig. 3. The outer ellipse is the unit circle and indicates 100% explained variance. The inner ellipse indicates 50% of explained variance. The variables close to each other have a positive correlation.

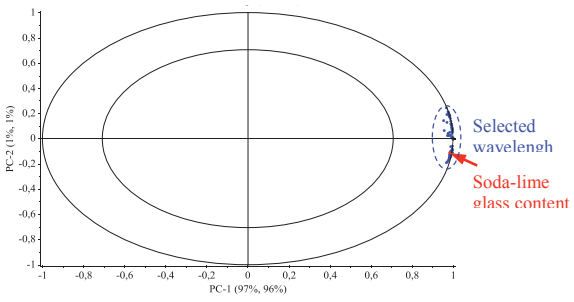

Fig. 3. Correlation loadings plot for a model No. 4

The PCR model No. 4 is presented in Fig. 4 as predicted Y value, i.e. soda-lime glass content from the model, against measured (reference) Y value. Blue dots represent the calibration data and red dots the test data.

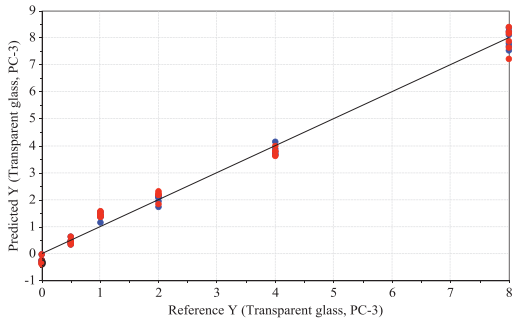

Fig. 4. PCR model No. 4 based on 1st derivative data, including selected wavelengths

Regression coefficients (Fig. 5.) summarize the relationship between all predictors and a given response. There are 81 predicting variables, which is equals to the number of selected wavelengths. Moreover, the plot indicates that wavelengths: 1794, 992, 994, 996, 998, 1072, 1000 (nm) are the most important for the prediction. These wavelengths can't entirely match with attributed absorption bands [27-29], since the data pretreatment (1st derivative) has been applied. The multivariate regression model equation is written as:

$$Y = B_0 + B_1 \cdot X_1 + B_2 \cdot X_2 + \cdots + B_{81} \cdot X_{81} \quad (1)$$

Where $B_0 = 93.3664$ and other regression coefficients B_1, B_2,…, B_{81} are presented in the plot.

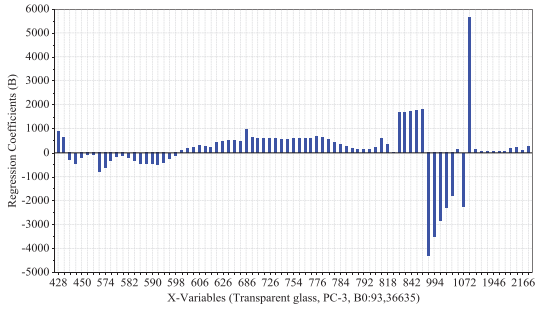

Fig. 5. Regression coefficients for the model No. 4

The glass detectability can be largely explained by an occurrence of overtones or harmonics of fundamental Mid-IR absorption bands in the NIR range. In the Mid-IR region, there are strong fundamental absorption bands attributed to Si-O-Si and O-Si-O bending and stretching modes at 16667 nm and 19800-25000 nm [28, 29].

4. Conclusions

NIR spectrometric experiments have been performed on biomass-based fuel samples containing soda-lime glass shards. Experimental results and multivariate statistical analysis show that the glass shards distributed in dry pine wood shavings are detectable. The best performing PCR prediction model developed achieve good prediction capability parameters (RMSEC = 0.2787 vol%, RMSEP = 0.3268 vol%, R^2_{cal} = 0.9901, R^2_{val} = 0.9876). Moreover, results from the PCR modeling shows that the most promising method of data pretreatment for development of PCR models is the 1st derivative when only absorbance spectral data from selected wavelengths are considered. Application of this pretreatment shows error improvements i.e. RMSEC and RMSEP, 40% and 35% respectively and R^2 improvements of approx. 1% compared to the model based on measured data pre-treated only with mean normalization. In summary, it has been demonstrated that glass in biomass-based material is quantitatively detectable by means of near-infrared spectroscopy. The model prediction performance can be improved by applying different data pre-processing techniques. The research work presented in this paper is intended to be complemented by acquiring spectra from a large number of additional samples that feature combinations of glass and biomass.

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Biography

Jan Skvaril is a PhD student at Mälardalen University, Sweden. He holds a master's degree in Mechanical Engineering and a master's degree in Economics and Management, both from Brno University of Technology. Currently he is studying the utilization of Near infrared (NIR) spectrometry for prediction, optimization and control of industrial applications.